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13. ABSTRACT (Maximum 200 words)

The goals of this program are to provide accurate kinetic data on isolated elementary reactions at temperatures relevant to Army combustion models, particularly for propellant combustion dark zones and also for development of halon replacements for fire retardation. Measurements have been made in high temperature photochemistry (HTP) reactors. Rate coefficient expressions over wide temperature ranges are reported for the reactions $O + N_2O \rightarrow O_2 + N_2$, $N + N_2O \rightarrow N_2 + NO$, $O + CHF_3 \rightarrow OH + CF_3$, $H + NO + Ar \rightarrow HNO + Ar$, $NH + CO_2 \rightarrow HNO + CO$. For the first of these reactions the relation to the alternate 2NO product channel is discussed. The potential impact of the results on the continuing development of Army models is considered. A statistical method has been developed for testing the exponentiality of noisy measurements in the time domain, such as are sometimes obtained in HTP and many other types of experiments.

14. SUBJECT TERMS
combustion models, nitramines, nitrate esters, dark zones, propellant combustion, fire retardants, reaction kinetics, temperature effects, O, N, H, NH.

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Table of Contents

I.   STATEMENT OF THE PROBLEM AND APPROACH

Models of the combustion of nitrate ester and nitramine propellants, especially those for dark zone structures, depend critically on chemical kinetic input data for individual reactions at the temperatures of interest. Under this grant we have obtained such data for sensitive reactions. We also report on a study of a fluorohydrocarbon oxidation reaction, in the context of halon-replacements for Army fire retardants. Two of our unique HTP (high-temperature photochemistry) reactors, Figs. 1 and 2,[1,2] have been used to provide the data. Such reactors operate in a wall-free pseudo-static mode, and the reactions are studied in isolation of other reactants. The 300 to 1800 K temperature regime can be covered. All rate coefficients in this report are in cm/molecule/s units. For the ΔH_{298} data, see Ref. 3.

In Section II of this report the results are discussed in terms of their significance to the Army. In Section III the more general scientific importance is emphasized.

II.   SUMMARY OF MOST IMPORTANT RESULTS

A reaction much faster than previously assumed.

N_2O is an important propellant combustion intermediate. Models are sensitive to its reactions with O-atoms. The reaction has two channels: production of 2 NO (a) and $N_2 + O_2$ (b). Till recently the accepted wisdom was that both reactions occur with essentially the same rate coefficients. Most studies on this reaction were made above 1700 K. No direct measurements were available at or near dark zone temperatures. A review by Anderson and Meagher at ARL showed that below 1700 K the prior studies involving this reaction had been misinterpreted.[4] Furthermore, no pertinent results could be extracted from those studies. Extrapolation to dark zone temperatures of results of a 1992 shock tube study by Davidson et al. suggested that $k_a + k_b$ is much larger there than previously assumed and that k_b is larger than k_a.[5] While the HTP technique was designed to go to higher temperatures than the traditional near room temperature techniques, in the present work it allowed us to go to lower temperatures, i.e., 1050 - 1300 K, than had been

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available to others. The results qualitatively agree with the extrapolation of the Davidson et al. study. Combined with the modeling study of Anderson and Meagher it is concluded that $N_2 + O_2$ production dominates in dark zones.[4] At e.g., 3000 K, the 2 NO channel dominates.

A reaction that does not need to be added to models.

The reaction between N atoms and N_2O is not considered in most models as it is spin-forbidden. However, observations elsewhere in a multi-reaction system could be interpreted that it proceeds rapidly, presumably to a spin-allowed excited product.[6] It was therefore recommended[6] that we study this process with our isolated reaction equipment. No reaction was observed and the models therefore do need not to be adjusted for this reaction.

A fire retardant compound reaction.

Fluorohydrocarbon compounds such as CHF_3 are being considered as part of a mixture of halon fire retardants replacements. Its reaction with major fire radicals need to be known to model the flame inhibition effects. The present work has supplied the necessary kinetic information on the reaction $O + CHF_3 \rightarrow OH + CF_3$.

Resolution of a discrepancy between high and low temperature data.

The H_2/N_2O chemical system represents an important subset of nitramine propellant combustion models. Accurate rate coefficients for H + NO recombination have been identified several times in recent years as needed for modeling this system.[7,8] There are conflicting measurements on this reaction: measurements in multi-reaction environments near 1000 K[8,9] yielded values three times lower than a recommendation[10] based on several older measurements. We have now studied the reaction from 295 through 906 K. Good agreement is obtained with the previous high-temperature data, but not with the older, lower temperature, results. Further analysis of the latter indicates that

the discrepancy is attributable to problems with the measurement techniques available for the older studies.

A reaction which may have to be added to models.

The reaction $NH + CO_2 \rightarrow HNO + CO$ was considered to be too slow to warrant inclusion in models, based on previous measurements. Our results indicate that it is faster and should be reconsidered for models.

III.   RESULTS AND PUBLICATIONS

A.   Published papers with abstracts

A. Fontijn, A. Goumri, A. Fernandez, W.R. Anderson, and N.E. Meagher, "Kinetics of the $O(^3P) + N_2O$. Reaction. 1. Direct Measurements at Intermediate Temperatures", Journal of Physical Chemistry A., 104, 6003 (2000).

Rate coefficients for the consumption of O atoms by reaction with N_2O have been measured, at pressures from 130 to 500 mbar, using the high-temperature photochemistry technique. These represent the first direct measurements of k values for the reaction. Ground-state oxygen atoms were produced by laser photolysis of SO_2, or by flash photolysis of either SO_2 or O_2, and monitored by time-resolved resonance fluorescence. The results yield k(1075 - 1140 K) = 3.2 x 10^{-11} exp(-9686 K/T) cm^3 molecule^{-1} s^{-1} with 2σ precision limits of $\pm$ 12% and corresponding 2σ accuracy limits of $\pm$26%. Results from several sources in the literature indicate a high sensitivity of the $O + N_2O$ reaction system to traces of H_2O, which increases the rates if present as a contaminant. For this reason, possible effects of traces of H_2O on the results were modeled. Simulated decay curves with a hypothetical H_2O contaminant were used as a test of the experimental data reduction procedures. Although the concentration of H_2O needed to significantly affect the results is small, the amount that could have been present is even less and is shown to have had negligible effects. The results are in qualitative agreement with a recent $T \geq$

1680 K shock tube study,[5] in that extrapolation of those results to the present temperatures indicates rate coefficients much larger than had been previously thought. However, though the results agree within error limits for such a long extrapolation, the present results are about a factor of 4 smaller. Combined with the results of the companion paper by Meagher and Anderson,[4] in which the prior literature is critically reevaluated, it is found that the $O_2 + N_2$ product channel dominates at the present temperatures.

A. Fernandez and A. Fontijn, "The $N(^4S) + N_2O(X^1\Sigma)$ Reaction", International Journal of Chemical Kinetics <u>33</u>, 387 (2001).

The title reaction, which is spin-forbidden for $N_2(X^1\Sigma_g^+) + NO(X^2\Pi)$ production, has been studied from 960 to 1130 K in a high-temperature photochemistry reactor. No reaction could be observed, indicating $k < 1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}. It is concluded that there is no significant contribution from the spin-allowed exothermic path leading to $N_2(X^1\Sigma) + NO(a^4\Pi)$.

A Fernandez and A. Fontijn, "Wide Temperature Range Kinetics of the $O + CHF_3$ Reaction", Journal of Physical Chemistry A <u>105,</u> 8196 (2001).

Rate coefficients for the depletion of ground-state oxygen atoms by CHF_3 have been measured using a high-temperature photochemistry (HTP) reactor. The O atoms were generated by the vacuum ultraviolet (vuv) flash photolysis of either SO_2, O_2, or CO_2, and their relative concentrations were monitored by resonance fluorescence. The data are best fitted by the expression $k(630 - 940 \text{ K}) = 2.5 \times 10^{-11} \exp(-7236 \text{ K}/T)$ cm^3 molecule^{-1} s^{-1}. The data are contiguous with those from an earlier laser-photolysis shock-tube study for temperatures ranging from 960 to 1330 K. A fit to the combined data yields the recommendation $k(630 - 1330 \text{ K}) = 5.1 \times 10^{-10} \exp(-9536 \text{ K}/T)$ cm^3 molecule^{-1} s^{-1}, with 2σ precision levels varying from ± 8 to $\pm 22\%$ and corresponding suggested accuracy levels of ± 22 to $\pm 29\%$. Transition-state theory predictions, made using input data from a literature ab initio study, are in excellent agreement with this recommendation over the entire temperature domain.

B.   Results yet to be published.

P.S. Riley and A. Fontijn, "The H + NO + Ar → HNO + Ar Reaction over a Wide Temperature Range".

Information on

$$H + NO + M \rightarrow HNO + M \qquad (1)$$
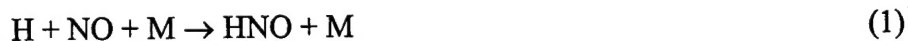
in the third-order regime comes predominantly from two types of experiments. The first are older experiments on elementary reactions with a series of bath gases, including H_2, Ar, but not N_2. Based on some of these Tsang and Herron[10] have inferred a k(T) expression for $M = N_2$. However, two recent studies[8,9] for $M = N_2$ near 1000 K in more complex environments indicated a value about 3 times lower than the recommendation. The present work was undertaken to cover this entire temperature range under isolated reaction conditions with one bath gas in one reactor.

An HTP (high-temperature photochemistry) reactor was used. H-atoms were generated by the vuv flash-photolysis of NH_3 and their concentration was monitored in fluorescence using a microwave-discharge flow lamp. Ar was the bath gas; attempts at use of N_2 led to unacceptably weak H-signals. The measured rates were divided by 2 to allow for the rapid follow-up step $HNO + H \rightarrow H_2 + NO$.

The measurements have been made at 295, 372, 501, and 906 K and pressures in the 30-425 mbar domain. The result is

$$k (295\text{-}906 \text{ K}) = 3.3 \times 10^{-34} \, (T/K)^{0.206} \exp (780 \text{ K}/T) \text{ cm}^6 \text{molecule}^{-2} \text{s}^{-1} \qquad (2)$$

with $\pm 2\sigma$ precision limits of 16% to 36% depending on temperature. Allowing conservatively for systematic errors of $\pm 20\%$ leads to $\pm 2\sigma$ accuracy limits of 29 to 42%.

In Fig. 3 this result is compared to literature data for $M = Ar$.[11-14] Also shown are $M = N_2$ data[8-10] divided by 1.6, the collision partner efficiency ratio from Campbell and Handy[14] for the 285-425 K range. The agreement thus suggested with Refs. 8 and 9 is excellent. At 1000 K eq. (2) gives a value 28% lower than the adjusted Glarborg

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expression. Eq. (2) gives much lower values than the previous low temperature M = Ar data. These involve [H]-measurement methods that can in view of later work be considered as unreliable for rate coefficient determinations, though not necessarily for relative third-body efficiencies, as will be discussed in the manuscript for publication being prepared.

It is suggested that eq. (2) be used instead of the previous recommendation. This expression can be multiplied by 1.6 for N_2 as the third body.

S.M. Shamsuddin and A. Fontijn, "Temperature Dependence of the $NH(X^3\Sigma^-)$ Reaction with CO_2".

Rate coefficients for

$$NH(X^3\Sigma^-) + CO_2 \rightarrow HNO + CO \tag{3}$$

have been measured using the apparatus of Fig. 2. The NH(X) was produced by the 193 nm two photon photolysis of NH_3 which produces $NH(A^3\Pi)$.[15] This species has a radiative lifetime of $4.2 \times 10^{-7} s$[16] so that on a time scale short compared to the experiments it is converted to $NH(X^3\Sigma^-)$. Simultaneously formed NH excited singlet molecules are rapidly quenched by the N_2 or N_2/Xe bath gas mixtures used. This novel production method was tested by making a few measurements on the NH(X) + NO reaction, which agreed within experimental uncertainty with previous studies, particularly the only other temperature-dependent results.[17] Our measurements varied from 72% of their value at 300 K to 91% of their result at 985 K. The NH radicals were monitored by laser-induced fluorescence on the NH(A - X) transition at 336 nm.

The data obtained on reaction (3) are shown in Fig. 4. The best -fit line shown corresponds to the expression $k_3(415 - 985 \text{ K}) = 1.9 \times 10^{-16} (T/K)^{1.12} \exp(-1894 \text{ K}/T) \text{ cm}^3$ molecule^{-1} s^{-1} with 2σ precision limits varying from $\pm 5\%$ to $\pm 7\%$ depending upon temperature, and corresponding 2σ accuracy limits of $\pm 21\%$. These results are compared in this figure to the shock-tube measurements by Rohrig and Wagner[18] which give $k_3(1200-1735 \text{ K}) = (1.8 \pm 0.8) \times 10^{-11} \exp[(-7220 \pm 200) \text{ K}/T]$. Extrapolations of

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these respective results to each others temperature ranges show appreciably higher values from the present work. Our measurements above 1000 K showed a much faster increase with temperature than the results below 1000 K. These higher temperature data appear suspect and, subject to further analysis, are not recommended or shown.

These results represent the final measurements on the present grant. No decision regarding publication has yet been made as we are considering combining them with results on proposed[19] further NH reactions. Thus, exploratory measurements on NH + N_2O have already shown that this reaction proceeds at considerable rates. There had been no previous measurements on it and it had been thought to be immeasurably slow. It is therefore not yet included in models.

A. Fernandez, "Validation of Noisy Exponential Decays"

In HTP experiments the decrease of the active species concentration is supposed to follow an exponential function. However, deviations from exponentiality could be obscured by a relatively large noise level. Attribution of exponentiality without the application of a suitable validation technique can lead to erroneous results. Visual observation of residuals plots usually can be used to recognize deviations from exponentiality. In our past work we have additionally used a computational runs test for objective validation. Some other laboratories use the Chi-square test, while most experimenters ignore the problem. We now have developed a new validation method, the bootstrap-validation technique, exponential model (BVTEM); it consists of a computer program that compares the deviation of the "test" decay to that of a suitable number of simulated exponential decays. If the test decay has a significantly large deviation, it is deemed to be non-exponential. The BVTEM was applied to decay data of two reactions, $N + O_2$ and $O + CHF_3$, and yielded at 14% and 8% rejection of decays which had previously passed the runs test, respectively. This did not affect the k(T) expressions obtained, but still implies that the BVTEM is more sensitive than the runs test. However, this claim is inconclusive since these data are experimental, i.e., unknown.

The three methods have now been tested by a statistical biasedness comparison test. It consisted of generating groups of 2000 exponential "test" decays, setting a

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significance level (probability of rejecting good data), and then applying the three validation techniques. This required the development of an automated version of the original computer program. The BVTEM was applied to each of these decays 500 times; this was established to be an adequate bootstrap replication size. Suitable groups of test decay data were considered: normal-, and Poisson-distributed residuals (i.e., noise) with S/N of 3.5-10. It was found that the BVTEM and the runs test are unbiased at a significance level of 0.5%. The Chi-square test was found to be biased and was thus discarded from further testing.

The second comparison, sensitivity to small departures from exponentiality, was performed by generating groups of 2000 non-exponential "test" data and applying the BVTEM and the runs test in the same fashion. Two types of non-exponential test data were used: a) double-exponential data and b) exponential data with a sinusoidal deviation. These input data have root mean square deviations from exponentiality ranging from 0.4 to 8%. Examples are shown in Figs. 5-7. When applied to some earlier studies, it was found that, on average, the BVTEM had a sensitivity roughly 9 times greater than that of the runs tests. In the study of the $NH + CO_2$ reaction it almost fully agreed with the residuals method.

One can conclude that the BVTEM is a preferred computational method for validating exponential decays. BVTEM can be extended to validation of data with a different functional dependence. A detailed description of this work will appear in Mr. Fernandez' Ph.D. Thesis, now being completed, and will be submitted for publication

IV.   PARTICIPATING SCIENTIFIC PERSONNEL

Dr. Arthur Fontijn, Abel Fernandez, Aleksandra Ristanovic, Laurie A. Chavasse, William F. Flaherty, Patrick S. Riley, Dr. Sayed Shamsuddin.

Ms. Ristanovic and Mr. Riley received their Masters Degrees in Chemical Engineering in, respectively, 2001 and 2002. Mr. Fernandez is expected to be granted his Ph.D. in December 2002.

Throughout this work we maintained close contact with Dr. W.R. Anderson in ascertaining that our reaction selections could have a direct impact on ARL models for propellant combustion. For the $O + N_2O$ reaction we collaborated with him and his postdoctoral fellow Dr. N.E. Meagher. We discussed fire retardation problems with Dr. A. Miziolek at ARL. He also helped us to obtain a cylinder of CF_3H.

V.   INVENTIONS

There are no inventions. Mr. Fernandez will be copyrighting the BVTEM computer program as part of his thesis.

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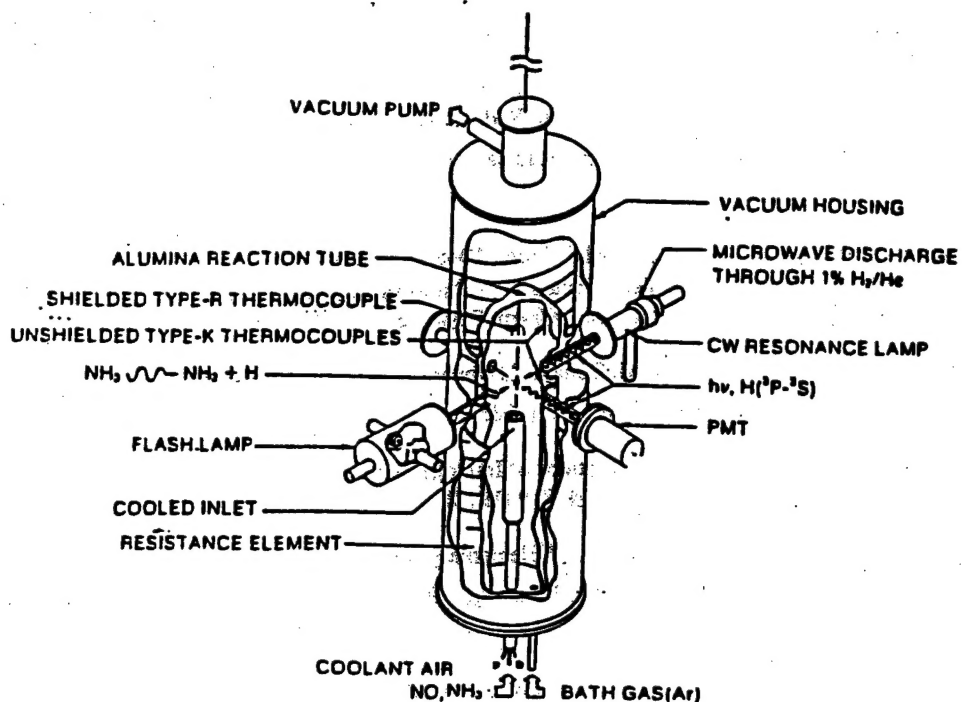
Figure 1   Schematic of HTP apparatus for atom reactions.
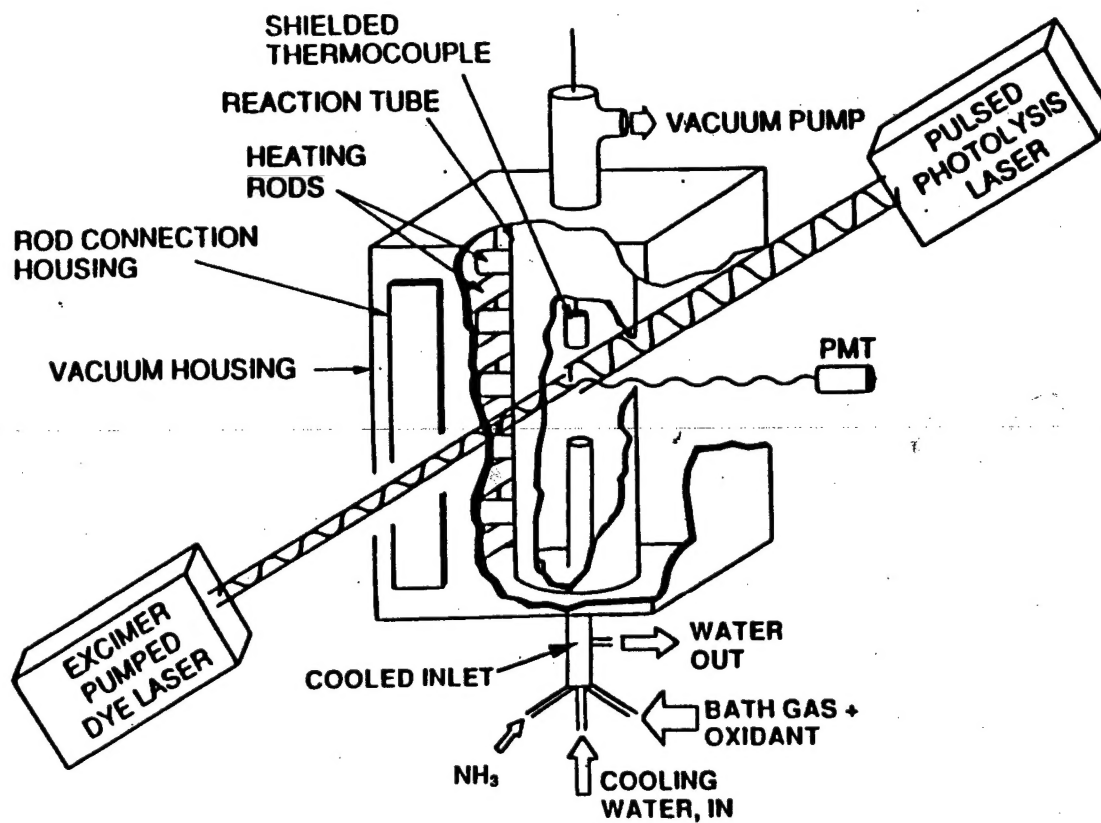It is shown as used for the H + NO + Ar study.

Figure 2   Schematic of the HTP reactor as configured for diatomic
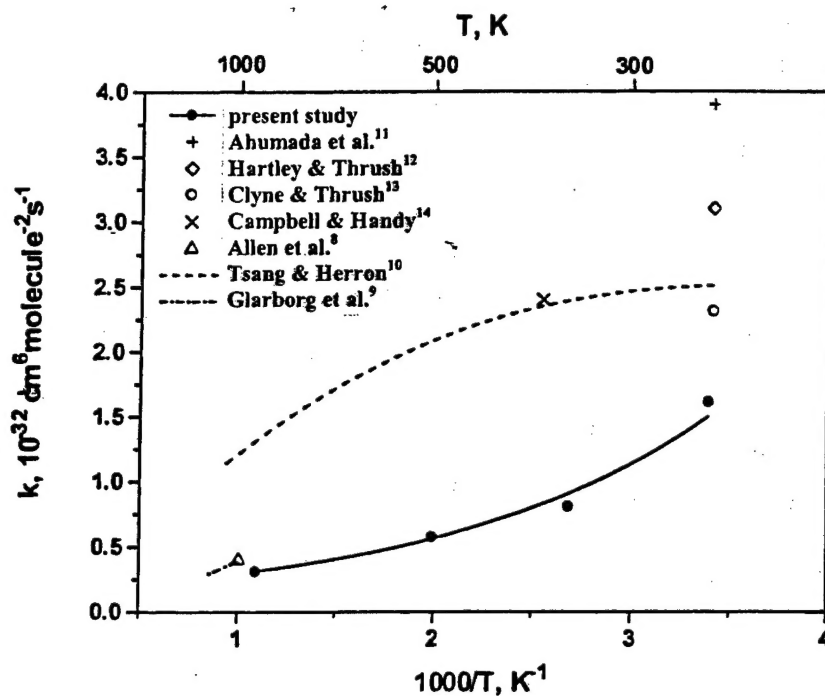transient reactants. It is shown as used for NH reactions.

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Figure 3   Comparison of the present H + NO + Ar results to earlier data. The Refs. 8 - 10 N_2 data have been adjusted to M = Ar.
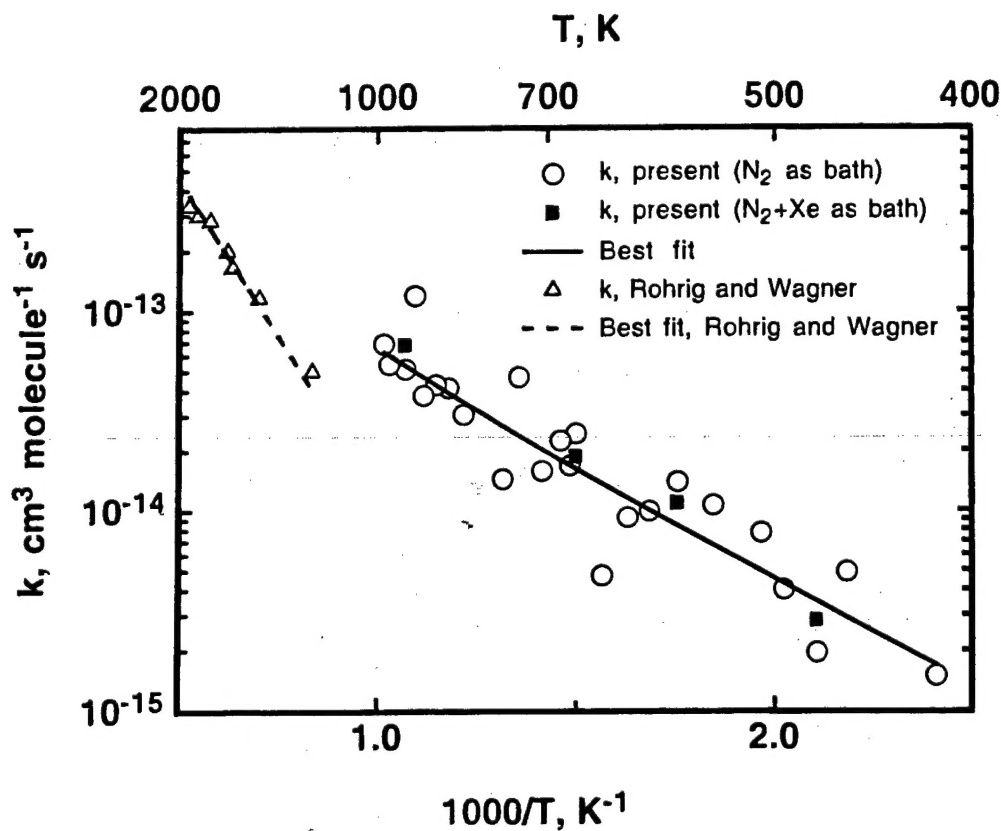
Figure 4   Summary of the results for the NH + CO_2 reaction. Also shown are the Rohrig and Wagner[18] data for this reaction.
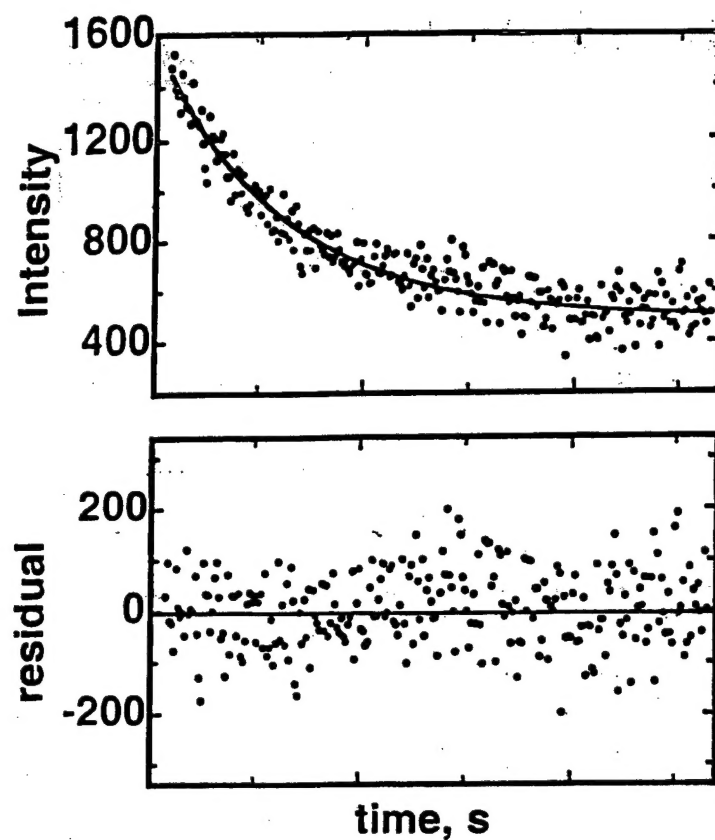
Figure 5   Normal distribution, non-exponential decay data, sinusoidal deviation, 3%, S/Sc = 3.5. Ratio.
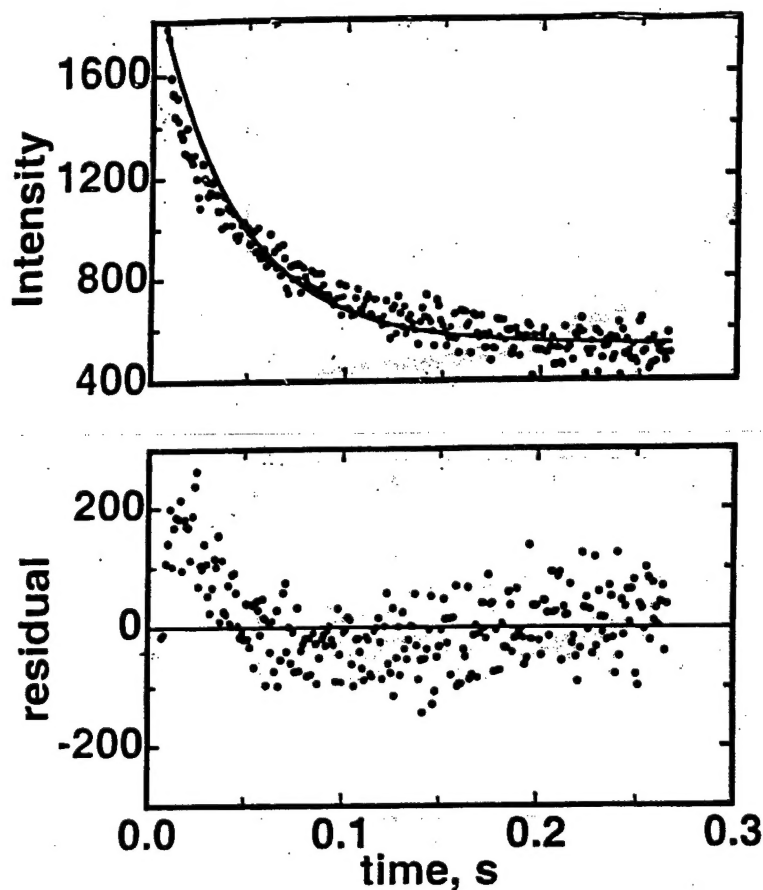

Figure 6   Normal distribution decay data, double exponential, 4.4% deviation, Noiseless data: Intensity = 1000 exp (-15t) + 500 + 1500 exp(-50t), S/Sc = 5. Ratio of BVTEM-to-runs test rejection ratio = 13.
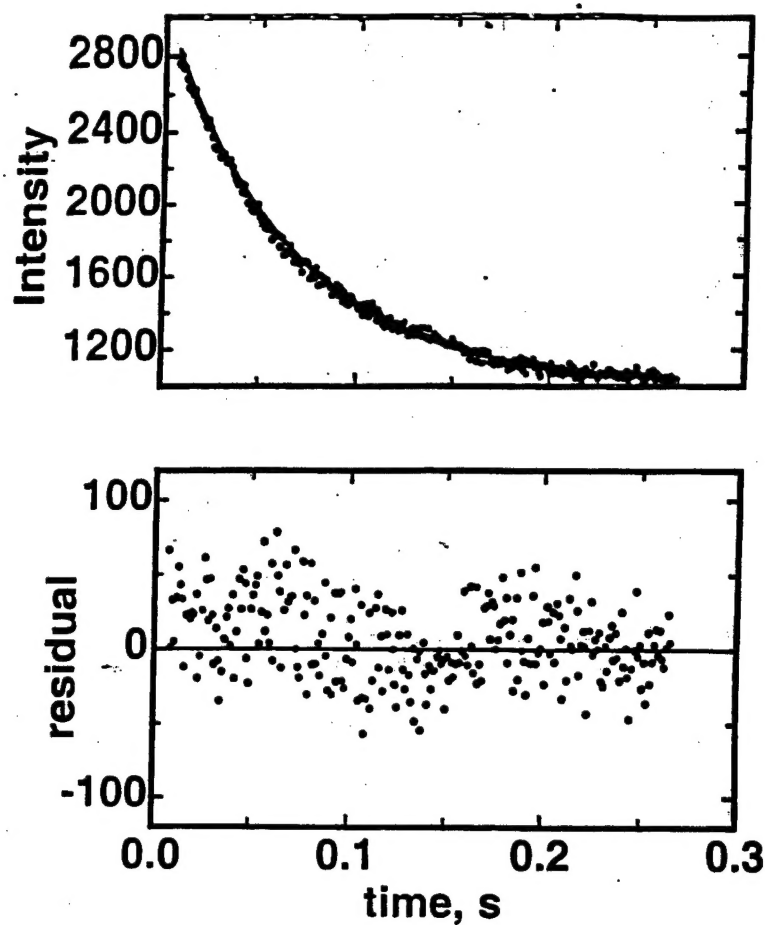
Figure 7   Poisson distribution non-exponential decay data, sinusoidal deviation, 0.8%, S/Sc = 19. Ratio of BVTEM-to-runs test rejection = 21.